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A Sulfur Segregation Study of PWA 1480, NiCrAl, and NiAl Alloys

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SUMMARY

Some nickel based superalloys show reduced oxidation resistance from the lack of an adherent oxide layer during high temperature cyclic oxidation. The segregation of sulfur to the oxide-metal interface is believed to effect oxide adhesion, since low sulfur alloys exhibit enhanced adhesion. X-ray Photoelectron Spectroscopy (XPS) was combined with an in situ sample heater to measure sulfur segregation in NiCrAl, PWA 1480, and NiAl alloys. The polished samples with a 1.5 to 2.5 nm (native) oxide were heated from 650 to 1100 °C with hold times up to 6 hr. The sulfur concentration was plotted as a function of temperature versus time at temperature. One NiCrAl sulfur study was performed on the same casting used by Browning (ref. 1) to establish a base line between previous Auger Electron Spectroscopy (AES) results and the XPS results of this study. Sulfur surface segregation was similar for PWA 1480 and NiCrAl and reached a maximum of 30 at% at 800 to 850 °C. Above 900 °C the sulfur surface concentration decreased to about 3 at% at 1100 °C. These results are contrasted to the minimal segregation observed for low sulfur hydrogen annealed materials which exhibit improved scale adhesion.

INTRODUCTION

Interfacial sulfur segregation has been related to the spalling of protective Al_2O_3 scales formed on NiAl and NiCrAl coating alloys as well as those formed on structural nickel based superalloys (refs. 1 to 8). Current research is now directed toward relating the bulk sulfur content of purified alloys to segregation potential and cyclic oxidation resistance. In an effort to demonstrate the importance of sulfur removal compared to the gettering effect of reactive element additions, various materials were processed to have less than 1 to 2 ppm sulfur. The dramatic improvements in cyclic oxidation resistance have been well documented (refs. 2, 6, and 7). However only a limited amount of segregation information is available for low sulfur alloys which indeed show minimal (1 percent) segregation for "high purity" NiCrAl (ref. 9). Furthermore we know of no published sulfur segregation data for the superalloys.

The primary purpose of this study is to document the sulfur segregation behavior of a commercially available single crystal PWA 1480 superalloy containing about 10 ppm sulfur. The segregation of the as-received superalloy was determined by hot stage XPS from 650 to 1100 °C and for hold times up to 6 hr. This was compared to the segregation behavior of the same material after desulfurizing to less than 1 ppm S by hydrogen annealing at 1200 °C for 100 hr. The results were compared to similar experiments for NiCrAl and NiAl.

EXPERIMENTAL PROCEDURE

Sample Preparation

The arc melted NiAl (88 ppm S), NiCrAl (13 ppm S), and vacuum induction melted polycrystalline PWA 1480 (11 ppm S) samples were fabricated into 1 cm diameter coupons 0.3 to 2 mm thick. The bulk composition of each sample is shown in table I. A second PWA 1480 sample (PWA 1480/H) was H₂ annealed for 100 hr at 1200 °C in 5% H/95% Ar forming gas. The bulk S concentration of PWA 1480 annealed under the same conditions in 100% H₂ was 0.3 wt% ppm (ref. 7). The surface of each sample was polished with 2400 SiC paper in water, rinsed with electronic grade methanol, and dried with nitrogen gas. The samples were mounted on a hot stage sample holder 1 cm ID by 3 mm deep (ref. 11). The samples were inserted in the vacuum chamber within 30 min after polishing. No sputter cleaning was performed, allowing the native oxide formed in room temperature air to remain on the sample. The sample heater has a Mo body with a W filament potted in alumina and is itself capable of 1400 °C. The samples were analyzed at room temperature and at 650 to 1100 °C in 50 °C steps for hold times of 1 to 6 hr.

Sample Analysis

The sample surfaces were characterized using XPS in a VG Scientific ESCALAB MkII with a five channeltron hemispherical analyzer and Mg α x-rays. The analyzer was operated in the constant analyzer energy (CAE) mode with a pass energy of 100 eV for survey spectra and 20 eV for the individual elemental spectra. A spot size of 5 by 2 mm was used.

Survey spectra were taken at the beginning and end of each experiment. Individual spectra were obtained for each element (table I) at room temperature and at the end of each heating experiment. The sample surface temperature was measured using an optical pyrometer calibrated with a type K thermocouple. During each time series at temperature the S 2p photoelectron peak was acquired in 4 to 12 min time intervals.

Spectra from individual elements were smoothed (ref. 12), the peak areas measured and normalized, and the binding energies determined. The normalized peak areas for each element were compared at the end of each time series at temperature and converted to an atomic percent. At temperatures before and after the loss of the native oxide, angle resolved XPS was used with 20° takeoff angles (ref. 13). This reduced the effective escape depth of photoelectrons by a factor of 3, making them comparable to AES electron escape depths. The sulfur peak areas obtained from sulfur profiles alone were converted to an atomic percent using the alloy compositions obtained at the beginning and end of each time series at temperature. The atomic concentration obtained in this manner assumes a homogeneous elemental distribution within the analyzed volume (5 by 2 mm, 2 to 3 nm deep). This is clearly not the case for sulfur concentrated at the metal-oxide interface, free metal surface, cavities and voids, or metal and oxide grain boundaries. However, the total concentration and chemical state of sulfur within the analyzed volume can be measured and compared for different samples.

RESULTS AND DISCUSSION

Sulfur Segregation on NiCrAl, PWA 1480, and NiAl

Previous AES sulfur segregation studies were performed on sputter cleaned NiCrAl surfaces (refs. 1, 4, and 8 to 10) with the oxide layer and all surface contamination removed. This was necessary because the AES electron escape depths were typically less than the native oxide thickness, preventing measurement of sulfur below or at the metal-oxide interface. Also, the model used for monolayer coverage of sulfur at a surface assumes that sulfur is present in a single overlayer at the free surface, allowing a determination of the degree of saturation at the free surface. In this study sulfur segregation was measured in the presence of a thin native oxide (1.5 to 2.5 nm).

The XPS depth of analysis is approximately three times that of AES allowing the metal-oxide interface to be seen through the native oxide. Figure 1 shows spectra obtained for Al 2p with both Al metal and Al oxide contributions. Since Al metal attenuated by the overlying oxide can be seen, the oxide metal interface is therefore detected. This allows the determination of differences in sulfur segregation behavior when the surface free energy and near surface stoichiometry have not been altered due to preferential sputtering and when the native oxide and metal-oxide interface are concurrently observed. Preferential sputtering has been shown to modify the normally Al-rich surface of NiAl and Ni₃Al to 90% Ni (ref. 14). All measurements were made here with the native oxide initially present.

The room temperature sulfur 2p spectrum is shown in figure 2. The chemical state of the room temperature sulfur (if present) was a sulphate. It was no longer present at 650 °C due to evaporation of SO_x species (ref. 2). From 650 to 1100 °C the sulfur, found as a metal sulfide, experienced little change in chemistry (ref. 10).

Sulfur segregation on the PWA 1480 alloy was first measured at 650, 800, 1000, and 1100 °C for hold times of 4 to 6 hr at temperature and is shown in figure 3. Sulfur, which was present at <1 at% at room temperature, segregated to about 1 percent at 650 °C for 2 hr, increased to a little over 1 percent after 5 hr at 800 °C. The native oxide was no longer seen at 1000 °C and sulfur concentrations increased to >8 percent within 1 hr and decreased to a steady state value of 5.5 to 6 percent over 2 to 6 hr. At 1100 °C sulfur concentrations decreased to 3 percent within 1 hr and remained at 3 percent for 2 to 6 hr. Thus 2 hr equilibration times at 50 °C increments were used in subsequent experiments.

The main results of this study are shown in figure 4. Here sulfur concentrations versus time at temperature are shown for NiCrAl, PWA 1480, and hydrogen annealed PWA 1480 (PWA 1480/H).

NiCrAl sulfur segregation.—The NiCrAl sulfur concentration was below XPS detection limits at room temperature. Sulfur segregation began at <650 °C and reached concentrations of 1 to 2 at% at 650 °C, 2.5 to 3 at% at 800 °C, 5 at% at 850 °C, 7 at% at 900 °C, and 7 to 8 at% at 950 °C. At 1000 °C sulfur decreased to 6 to 7 at%. However, at 1050 °C the native oxide was lost and the sulfur concentration increased to >8 at%. At 1100 °C with no oxide sulfur decreased to 3 at%.

The NiCrAl sulfur concentrations peaked at a value of 8 at% immediately following the loss of the native oxide at 900 to 1000 °C. From these results, a significant increase in sulfur concentration was found after the native oxide was gone indicating as others have seen (refs. 10 and 15 to 17) that sulfur concentrates at the metal-oxide interface. It has previously been shown that sulfur can be present within oxide grain boundaries but not in the oxide lattice itself (ref. 16).

PWA 1480 and PWA 1480/H sulfur segregation.—As with NiCrAl, no sulfur was seen at room temperature for the PWA 1480, but <1 at% sulfur was seen for the PWA 1480/H. Sulfur segregation for the PWA 1480 was similar to the NiCrAl. Although, the sulfur segregation at 850 °C rapidly increased to 9 at% concurrent with loss of the native oxide. At 900 °C the PWA 1480 sulfur concentration reached a maximum of >10 at%, decreased to 6 to 7 at% at 1000 °C, and reached 3 to 4 at% at 1100 °C. In comparison, the PWA 1480/H, which began with <1 at% at room temperature, showed no sulfur segregation below 900 °C. At 900 °C sulfur concentrations increased to 0.5 to 1 at%. At 950 °C the native oxide layer was lost and the sulfur concentration increased to 1.0 at%. The PWA 1480/H sulfur concentration reached a maximum of 1.2 at% at 1000 °C and decreased to zero at 1100 °C. The lack of segregated sulfur at 1100 °C for PWA 1480/H indicates that the PWA 1480 and NiCrAl, with 3 at% sulfur at 1100 °C, are continuously resupplied with sulfur from the bulk. Otherwise, the sulfur lost on the PWA 1480/H should also be lost for the NiCrAl and PWA 1480.

Angle resolved XPS (ARXPS) measurements were taken before and after the disappearance of the native oxide as shown in table IV. ARXPS at 70° off normal electron takeoff angles effectively decreases the depth of analysis by a factor of 3. The sulfur concentration increased by a factor of 3 to >24 at% at 70° off normal once the oxide was removed. This value can be compared to previous AES studies which claim saturation values at these temperatures of 15 to 38 at% on the sputter cleaned free surface (refs. 1, 8, and 10). At temperatures greater than 900 to 1000 °C, sulfur decreased either from increased bulk solubility or evaporation (refs. 18 and 19). No evidence was found to conclude that the sputter cleaned surface significantly altered the temperature dependence for segregation. The sulfur decrease seen at higher temperatures is apparently suppressed due to the oxide overlayer. XPS and AES are not precise enough to critically compare absolute sulfur concentrations, however the kinetic and temperature dependencies were similar.

The NiAl sample with 88 atomic ppm sulfur intentionally added showed surprisingly low segregation concentrations of 1 to 2 at% at temperatures below 900 °C and no sulfur at temperatures of 1100 and 1200 °C. This may indicate that segregation in NiAl is much less pronounced than on NiCrAl alloys as suggested by others (ref. 10). In any case, it is important to note that spallation is observed for this alloy with minimal segregation.

A comparison of the sulfur segregation behavior of PWA 1480 and PWA 1480/H show that clear differences exist. The PWA 1480/H alloy showed no segregation below 900 °C and only reached a maximum sulfur concentration of 1/10 the value reached by unannealed PWA 1480. At 1100 °C the PWA 1480/H had no sulfur at the surface. From these results a comparison is now made between sulfur segregation, bulk sulfur content, and cyclic oxidation behavior (ref. 7).

Sulfur Segregation versus Cyclic Oxidation Behavior for PWA 1480

In an earlier study on the effect of sulfur on scale adhesion (ref. 7), near zero specific weight changes were observed after 200 hr at 1100 °C for the PWA 1480 samples H₂ annealed at 1200 and 1300 °C (fig. 5). Also, the cumulative spall areas during the progress of 1100 °C cyclic oxidation tests were measured. Figure 6 shows that samples hydrogen annealed at 1000 °C showed cumulative spall areas up to 120 percent while samples annealed at 1200 and 1300 °C showed cumulative spall areas of only 1 percent or less. Thus, figures 5 and 6 show that H₂ annealing produces a significant improvement in the cyclic oxidation behavior of PWA 1480.

The improved cyclic oxidation behavior for hydrogen annealed PWA 1480 has previously been associated with the reduction in the bulk sulfur content (ref. 7). However, it has not been demonstrated whether the reduction of bulk sulfur would correspondingly reduce sulfur segregation. Figure 4 showed no sulfur segregation at temperatures $<950^{\circ}\text{C}$ and significantly reduced segregation at higher temperatures. A summary of cyclic oxidation, bulk sulfur content, and sulfur segregation results are shown in table II. From these results it was concluded that cyclic oxidation behavior is significantly improved by hydrogen annealing, which has now been shown to reduce both the bulk sulfur content as well as the interfacial segregation potential. Thus reducing the bulk sulfur content reduces the sulfur segregation at the oxide-metal interface, believed to weaken this bond (ref. 20).

Chemical Changes Associated With Sulfur Segregation

In an attempt to correlate sulfur segregation with other changes in the substrate chemistry, all elements of table I along with carbon and oxygen were measured at the end of each heating cycle. Tables III to V show the atomic concentration of these species for NiCrAl, PWA 1480, and PWA 1480/H. Angle resolved XPS (ARXPS) before and after removal of the oxide layer are also shown for the PWA 1480 sample.

NiCrAl composition and chemistry.—Table III shows the change in composition after 1 hr at each temperature. The room temperature as-polished surface was composed of Ni, Cr, and Al oxides. Carbon was also present at 30 at% composed of adventitious hydrocarbons and C-O species. At 650°C sulfur segregated to the near surface region and was present as a metal sulfide. The binding energy of sulfur 2p was consistent with Cr_2S_3 and NiS but could not be confirmed from the corresponding metal spectra. The binding energy of sulfur decreased from 650 to 1100°C consistent with a change from Cr_2S_3 to NiS while no chemical change was observed for the other elements in this temperature range. The oxide layer, composed of alumina at $>650^{\circ}\text{C}$, disappeared between 1 and 2 hr at 1050°C . Chromium increased between 800 and 850°C from 4 to 11 at% and then was depleted to 3 at% when the oxide disappeared. The Ni was low between 850 and 1050°C and increased with the decrease in Cr, producing a nearly stoichiometric NiAl phase with 3 at% Cr and S at 1100°C .

PWA 1480 and PWA 1480 H_2 annealed—The effects of heating on the overall PWA 1480 and hydrogen annealed PWA 1480 surface compositions are summarized in tables IV and V, respectively. The room temperature Ni, Cr, and Al composition of PWA 1480 was similar to NiCrAl. The native oxide was lost between 800 and 850°C and was associated with a factor of 2 increase in Ti, Co, W, and Ta, while Cr remained the same. The Al decreased a factor of 2 with the oxygen loss, while Ni, no longer being attenuated by the oxide overlayer, increased by a factor of 5. Major compositional changes are shown for both PWA 1480 and hydrogen annealed PWA 1480 in figures 7 to 9. This data was obtained after 2 hr at temperature.

Figure 7 shows the oxygen and sulfur concentrations versus temperature. The hydrogen annealed alloy lost oxygen at 1000°C compared with 850°C for the unannealed alloy. The sulfur concentration reached a maximum value immediately following the loss of the oxide in both cases. The sulfur began to decrease at 900°C for PWA 1480 with no oxide but did not decrease on the hydrogen annealed alloy until the oxide was also gone. This indicates the possible trapping of sulfides at the metal-oxide interface.

The concentrations of Ni, Cr, Al, and O versus temperature for PWA 1480 are shown in figure 8. From 850 to 1100°C Ti, W, and Al remained constant. Ta slowly increased with temperature. Cr and Co decreased with no Cr above 1000°C . Ni increased with the decrease in Cr with the Ni:Al ratio consistent with Ni_3Al at 1100°C . No chemical changes were observed once the native oxide was gone. The

sulfur chemical state was similar to that found on NiCrAl. The PWA 1480/H shown in figure 9 showed no difference in chemistry from the PWA 1480 with the exception of the presence of sulfur as a sulphate at room temperature, the lack of sulfur segregation below 900 to 1000 °C, and the native oxide stable up to 950 to 1000 °C. No explanation is apparent for the increased temperature at which the oxide disappeared.

To summarize, the changes in composition are primarily affected by the presence of the native oxide.

CONCLUSION

X-ray photoelectron spectroscopy allows the chemistry and composition of the oxide-metal interfacial region to be determined. Sulfur segregation was present on all alloys studied. Total sulfur concentrations reached values of 8 to 10 at% from the normal exit data and 25 to 30 at% at grazing exit angles for the PWA 1480 and NiCrAl samples after loss of the native oxide. This is consistent with previous Auger data in which values of 30 at% were reported for NiCrAl and is consistent with the assumption that the Auger sampling depth is 1/3 that of XPS. Total sulfur concentrations on the PWA 1480/H initially began at 0.5 at% and never exceeded 1.2 at%. No sulfur was seen at 1100 °C. The low concentration of segregated sulfur on the PWA 1480/H sample was correlated with reduced bulk sulfur content and improved cyclic oxidation behavior.

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TABLE I.—BULK COMPOSITION OF EACH ALLOY ATOMIC PERCENT

	S, ppm	Ti	Co	W	Ta	C	O	Al	Cr	Ni
NiAl	88	-----	-----	-----	-----	---	---	50	-----	50
NiCrAl	13	-----	-----	-----	-----	---	---	24	14.5	61.4
PWA 1480	11	1.63	6.12	1.08	3.32	---	---	9.36	12.72	65.76
PWA 1480/H	0.3 to 1	1.39	5.96	1.12	3.35	---	---	8.53	11.65	68.00

TABLE II.—SULFUR AND OXIDATION COMPARISON FOR PWA 1480
AND HYDROGEN ANNEALED PWA 1480

Sample	Weight change, mg/cm ²	Cumulative spall area, percent	Bulk sulfur content, ppm	Surface segregation concentration, percent
PWA 1480 control	-8	120	11	XPS, >10 70° ARXPS, >30
PWA 1480 H ₂ annealed	+0.3	1	0.3 to 1	XPS, 1

TABLE III.—NiCrAl ELEMENTAL CONCENTRATION (at%)
VERSUS TIME AT TEMPERATURE

Test conditions	S 2p	Ni 2p ₃	Cr 2p ₃	Al 2p	O 1s	C 1s
As polished,						
Room temperature	----	14	5.5	16	36	29
650 °C/1 hr	1.6	9.5	3.5	42	37	6.5
800 °C/1 hr	2.5	9.2	3.8	45	39	-----
850 °C/1 hr	5.2	14	11	42	28	-----
900 °C/1 hr	7.1	15.3	12	41	25	-----
950 °C/1 hr	7.0	16	13	41	23	-----
1000 °C/1 hr	6.9	17	12	41	23	-----
Overnight,						
1000 °C/1 hr	6.2	18	13	40	22	-----
1050 °C/1 hr	5.8	27	8.7	38	20	-----
1050 °C/2 hr	7.7	40	8.0	45	---	-----
1100 °C/1 hr	3.4	49	2.8	45	---	-----

TABLE IV.—ELEMENTAL CONCENTRATION (at%) VERSUS TIME
AT TEMPERATURE FOR PWA 1480

	S 2p	Ti 2p ₃	Co 2p ₃	W 4f	Ta 4f	C 1s	O 1s	Al 2p	Cr 2p ₃	Ni 2p ₃
Room temperature	----	----	----	----	----	33	42	6.9	5.6	13
650 °C	0.6	3.2	2.5	0.9	3.5	3.2	39	31	5.7	11
800 °C	2.1	2.1	3.2	1.7	3.8	2.7	31	33	11	9.3
800 °C 70° off	3.4	1.7	2.7	1.8	2.8	3.7	36	33	7.4	7.2
850 °C	7.9	4.1	6.8	2.3	5.7	----	----	18	11	45
850 °C 70° off	22	6.1	4.8	3.3	4.0	----	----	13	15	32
900 °C	7.8	4.2	5.4	2.8	5.8	----	----	18	8.2	48
900 °C 70° off	24	6.2	4.3	3.0	3.8	----	----	15	14	30
950 °C	7.3	3.1	4.7	2.6	6.8	----	----	19	4.0	53
1000 °C	6.6	3.4	6.4	2.7	7.3	----	----	20	----	54
1050 °C	4.7	4.6	3.8	2.6	7.8	----	----	21	----	56
1100 °C	1.3	4.0	3.0	2.3	8.6	----	----	21	----	56

TABLE V.—PWA 1480 ELEMENTAL CONCENTRATION (at%) AFTER H₂ ANNEAL
100 HR AT 1200 °C

	S 2p	Ti 2p3	Co 2p3	W 4f	Ta 4f	C 1s	O 1s	Al 2p	Cr 2p3	Ni 2p3
Room temperature	0.3	0.2	2.0	0.3	2.3	26	46	7.4	3.3	13
800 °C	0.3	2.0	2.4	0.8	3.7	6.2	39	32	4.4	9.3
850 °C	0.4	1.5	4.1	1.0	3.5	2.0	33	31	7.9	17
900 °C	0.7	1.1	5.3	1.4	3.4	----	29	30	9.0	21
950 °C	1.0	1.1	4.5	1.7	4.2	----	21	26	11	31
1000 °C	1.2	3.5	7.0	1.8	7.3	----	2.7	19	2.3	55
1100 °C	----	2.6	2.4	1.8	10.3	----	----	23	----	60

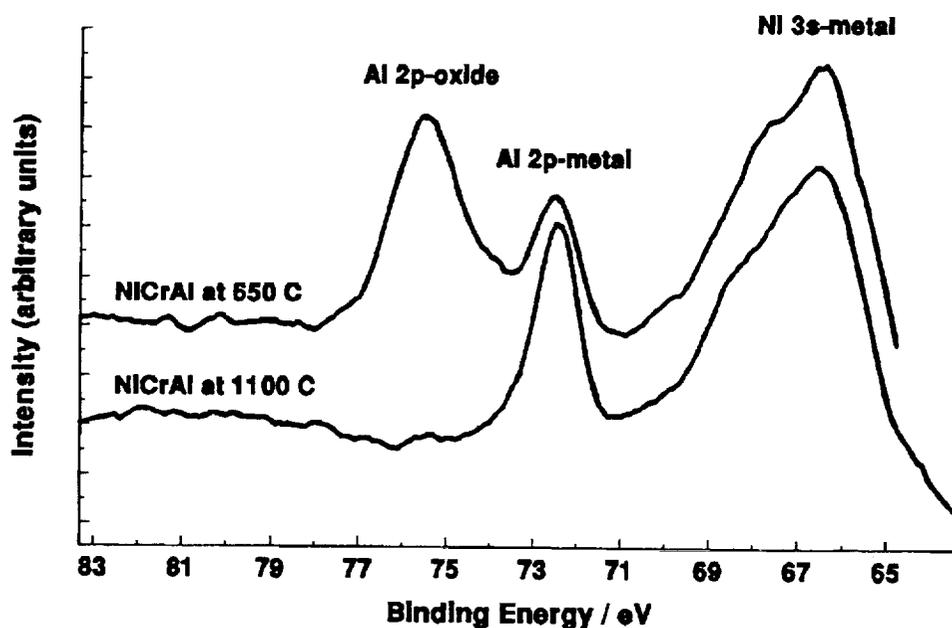


Figure 1.—Al 2p and Ni 3s spectra with and without the native oxide showing the difference between the Al oxide and Al metal.

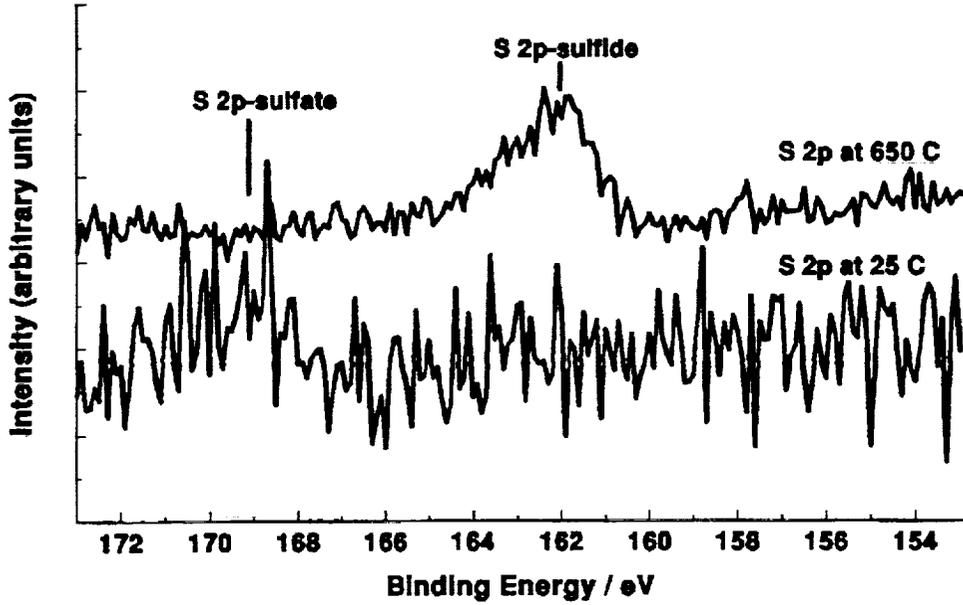


Figure 2. —Sulfur 2p spectra obtained at room temperature and at elevated temperatures. The room temperature sulfate was gone at 650 °C. The metal sulfide found at higher temperature decreased in binding energy with increased temperature.

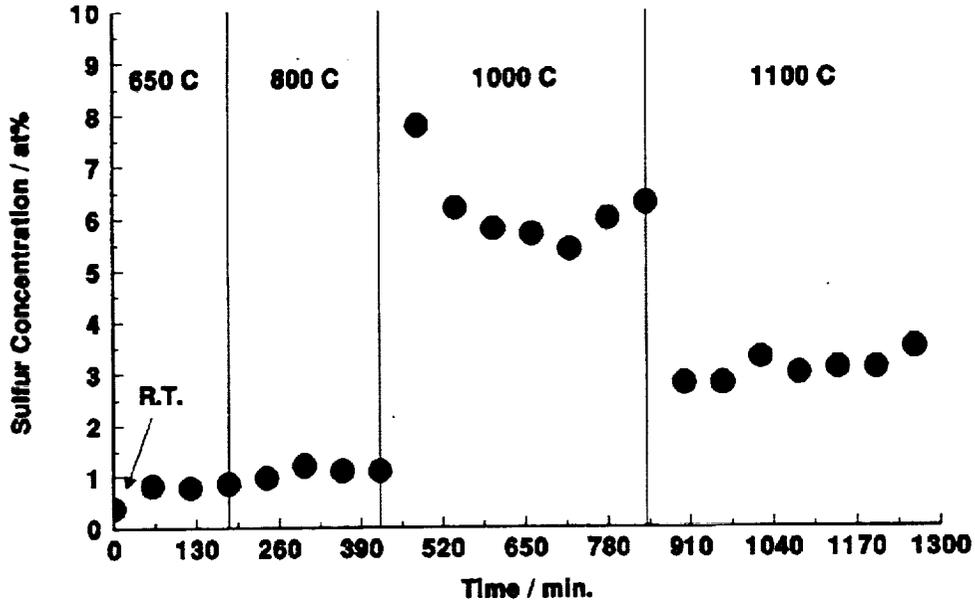


Figure 3. —The sulfur concentration of PWA 1480 vs time at temperature. After 1-2 hours at each temperature the sulfur concentration reached a steady state value. The native oxide was lost between 800-1000 °C.

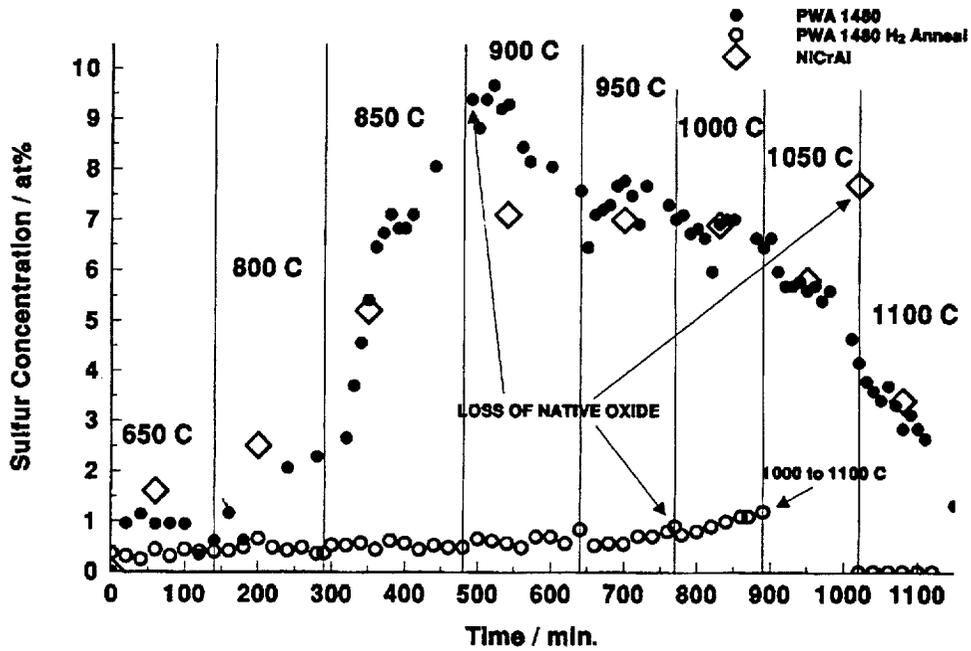


Figure 4. —A comparison of sulfur concentrations at temperature vs time at temperature for NiCrAl, PWA 1480, and H₂ annealed PWA 1480. The H₂ annealed PWA 1480 sulfur concentrations are significantly lower than the as-received PWA 1480.

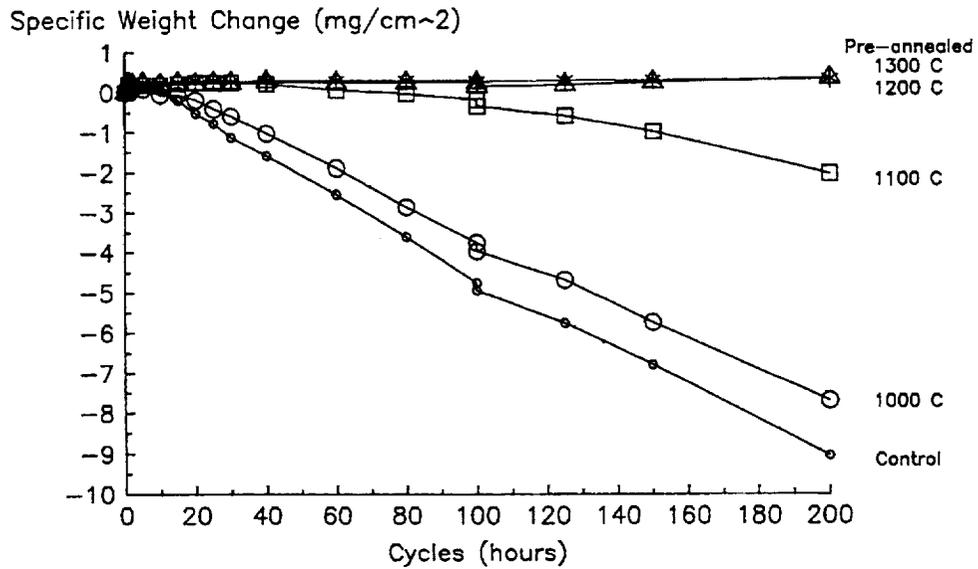


Figure 5. — The effect of H₂ annealing on cyclic oxidation. PWA 1480 polycrystalline. (1100 °C, 1-hr cycles) [7].

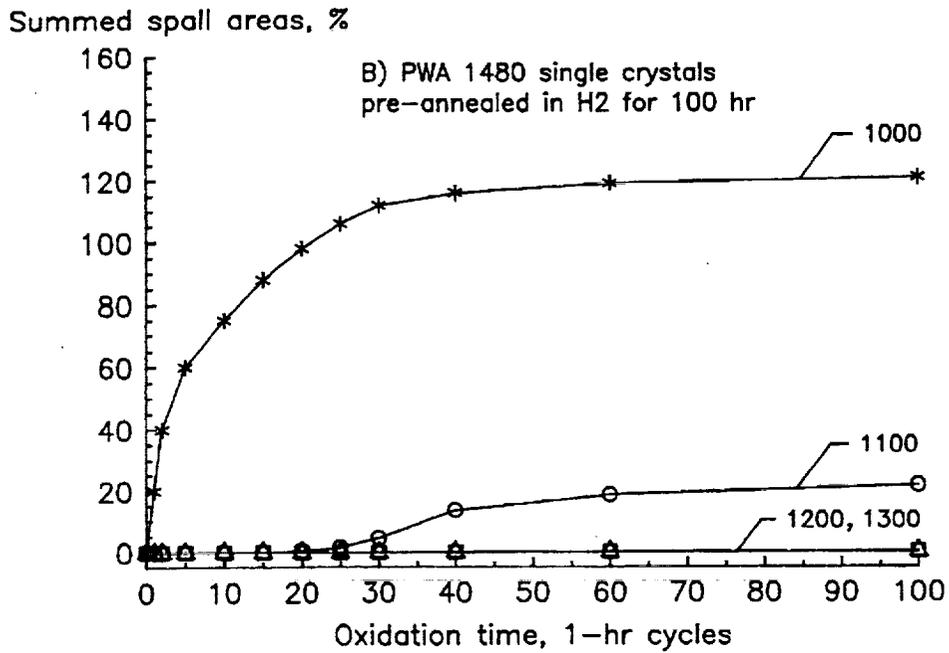


Figure 6. —Cumulative spall areas during 1100 °C cyclic oxidation (visual estimate of exposed metal surface) [7].

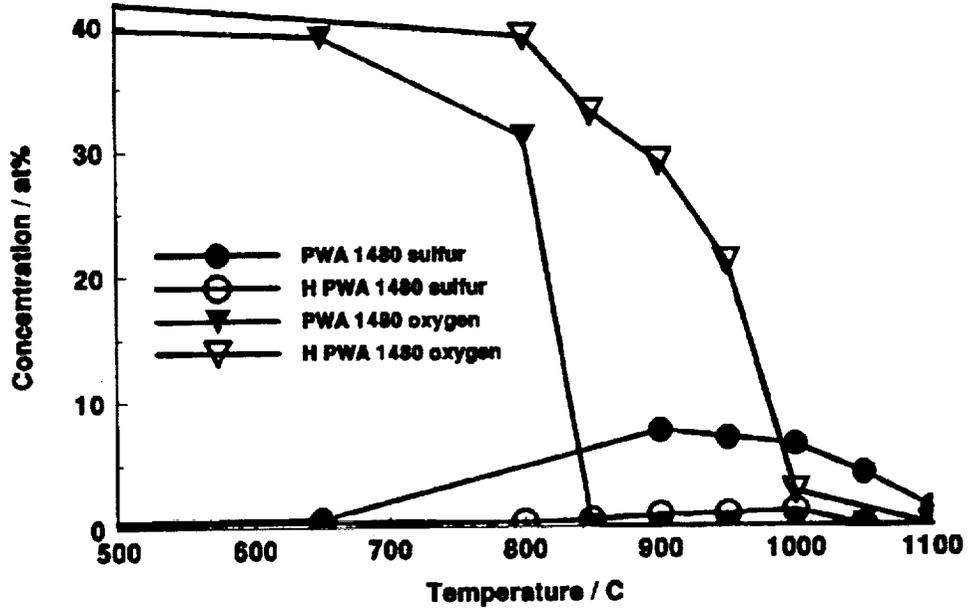


Figure 7. —Sulfur and oxygen concentration after two hours at each temperature for PWA 1480 before and after the H₂ anneal.

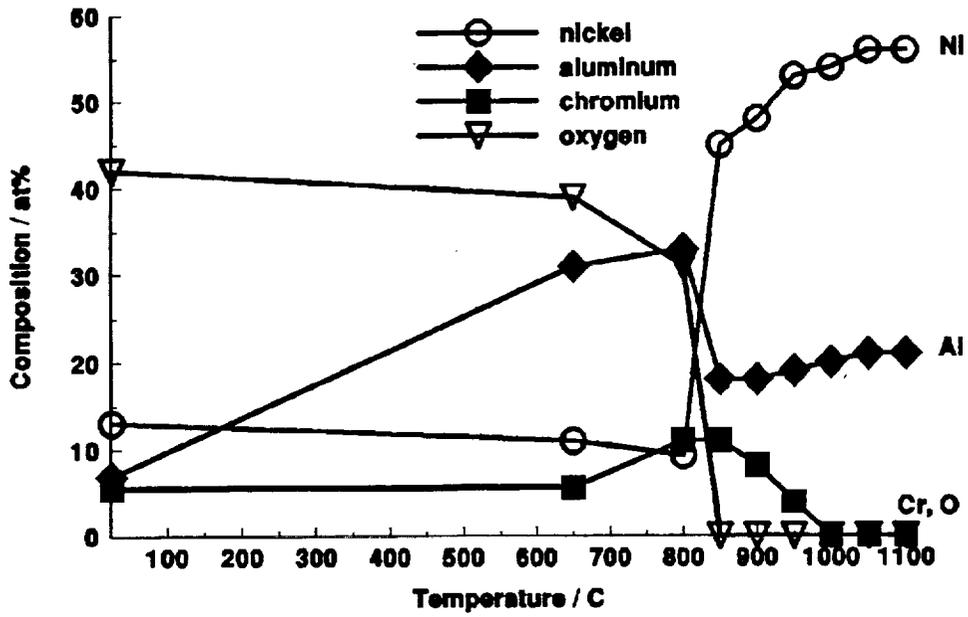


Figure 8. — Ni, Cr, Al, and O concentrations for PWA 1480.

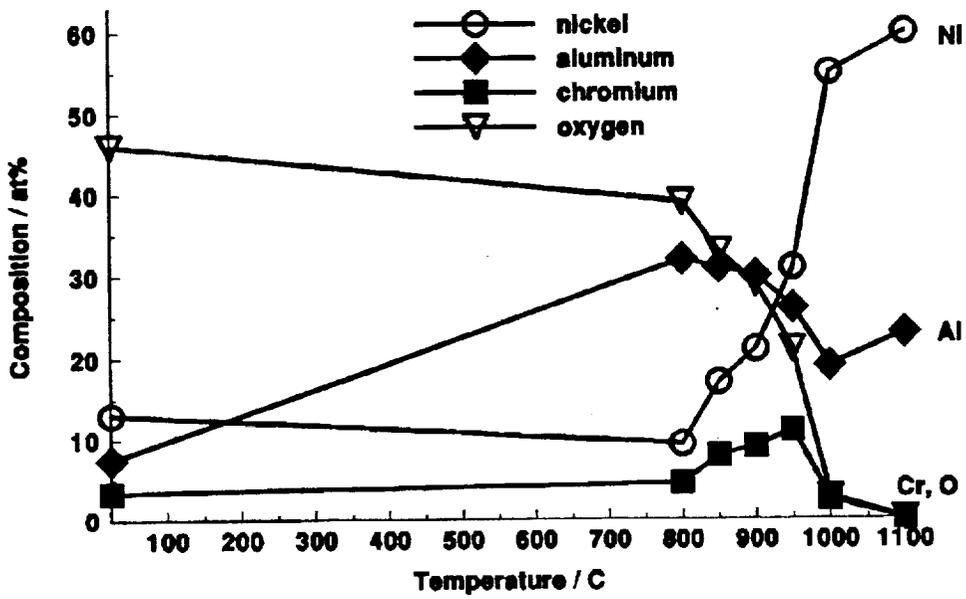


Figure 9. — Ni, Cr, Al, and O concentrations for PWA 1480 after hydrogen annealing at 1200 °C for 100 hrs. The composition was measured after two hours at each temperature.

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13. ABSTRACT (Maximum 200 words) Some nickel based superalloys show reduced oxidation resistance from the lack of an adherent oxide layer during high temperature cyclic oxidation. The segregation of sulfur to the oxide-metal interface is believed to effect oxide adhesion, since low sulfur alloys exhibit enhanced adhesion. X-ray Photoelectron Spectroscopy (XPS) was combined with an in situ sample heater to measure sulfur segregation in NiCrAl, PWA 1480, and NiAl alloys. The polished samples with a 1.5 to 2.5 nm (native) oxide were heated from 650 to 1100 °C with hold times up to 6 hr. The sulfur concentration was plotted as a function of temperature versus time at temperature. One NiCrAl sulfur study was performed on the same casting used by Browning (ref. 1) to establish a base line between previous Auger Electron Spectroscopy (AES) results and the XPS results of this study. Sulfur surface segregation was similar for PWA 1480 and NiCrAl and reached a maximum of 30 at% at 800 to 850 °C. Above 900 °C the sulfur surface concentration decreased to about 3 at% at 1100 °C. These results are contrasted to the minimal segregation observed for low sulfur hydrogen annealed materials which exhibit improved scale adhesion.				
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